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Ultrafast relaxation of the fundamental vibrations of SH^- and OH^- in potassium halides

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Abstract

The vibrational relaxation times of SH^- and OH^- in potassium halides, measured by incoherent laser saturation, vary from 0.8 to 7 ns at 1.7 K. A librational side band at $+300\text{ cm}^{-1}$ provides a possible decay channel. The strength of this mode is strongly temperature dependent, possibly owing to barrier hopping.

1. Introduction

Previously [1], we have found that the fundamental vibrations of SH^- doped in potassium halides decay at 1.7 K in a few hundred picoseconds. This was very surprising in light of the millisecond decay times found for the nominally-similar diatomic, CN^- , in the same hosts. We showed that a multiphonon-decay scheme is unable to account for these ultrafast SH^- decay rates, as expected since a large number of Debye phonons would be required to match the vibrational energies. In this paper, we describe experiments on OH^- which show that these diatomics also decay extremely rapidly, in a few nanoseconds at 1.7 K. In seeking an explanation for these results, we notice that previous spectroscopic studies [2] indicate that OH^- possesses a $\sim 300\text{ cm}^{-1}$ librational mode, in contrast with the $\sim 15\text{ cm}^{-1}$ librational mode [3] of CN^- . It is possible that the vibrations ultimately decay into librations at sufficiently low energies. In

order to examine this possibility, we have measured the spectra of SH^- at 0.5 mol% concentration and find a side band mode at around the same frequency of $+300\text{ cm}^{-1}$. A frequency shift of $\sqrt{2}$ is found for this line in a spectrum of SD^- , confirming its identification as a librational mode. However, the line strength is found to decrease rapidly with increasing temperature, perhaps indicating a crossover at higher energies from librations to other modes of motion.

2. Saturation results for OH^-

We generate tunable infrared laser pulses by difference-frequency mixing of Nd^{3+} :YAG and tunable dye-laser radiation in a LiNbO_3 crystal, as described in Ref. [1]. This laser system is used to saturate the $\nu = 0 \rightarrow 1$ transition of OH^- molecules doped at low concentrations (100-150 ppm) in potassium halide crystals, by varying the intensities of the incident pulses after tuning the laser frequency to the peak of the sample absorption line. For

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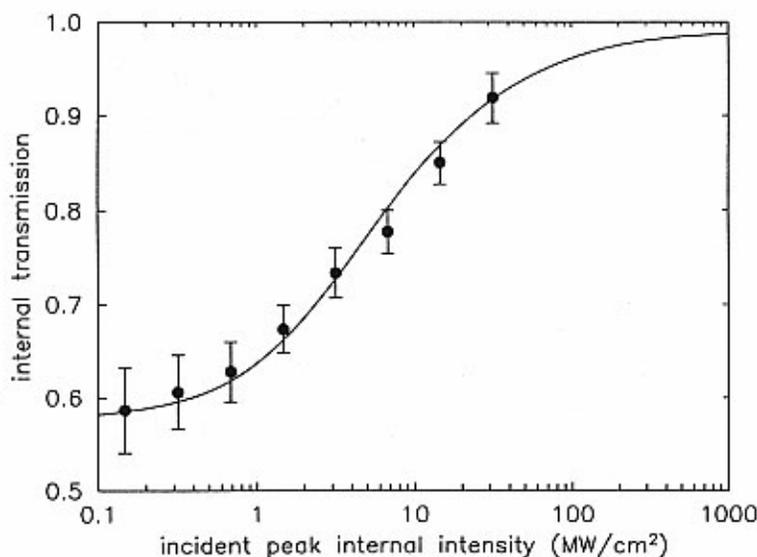


Fig. 1. Transmission of a KCl + 100 ppm KOH sample as a function of the incident laser intensity. Experimental data are indicated by the dots and the curve is obtained using a rate equation analysis with $T_1 = 5$ ns.

Table 1
Energy relaxation times at 1.7 K measured by incoherent saturation

Host	T_1 for SH^-	T_1 for OH^-
KCl	750 ps	5 ns
KBr	850 ps	7 ns
KI	2400 ps	-

example, Fig. 1 shows saturation results for KCl:OH⁻. The experimental points and error bars were obtained by measuring the transmission for several thousand laser shots with varying pulse intensities, dividing the intensity axis into bins, and averaging together the data points within each bin.

Owing to the large anharmonic shift, $2\omega_e x_e$, of 170 cm^{-1} in the vibrational ladder of OH⁻ [2], the incident radiation is only resonant with the $\nu = 0 \rightarrow 1$ transition, so that the molecule can be treated as a two-level system. We apply an incoherent rate equation analysis to determine the transmission of the laser pulses through the crystal [1]. The value of the energy relaxation time, T_1 , for each host was then varied until a best fit to the saturation data was found; for example, the fitted saturation curve

for KCl:OH⁻ is presented in Fig. 1. The results are summarized in Table 1.

3. Librational side bands

As we demonstrated previously [1], these extremely rapid relaxation rates for SH⁻ cannot be explained on the basis of a multiphonon decay scheme. In considering what else might account for the results, we were led to search for other modes in the sample absorption spectra. We discovered a broad line on the high-frequency side of the fundamental vibrational mode, ν_{01} , at $+331\text{ cm}^{-1}$ for KBr:SH⁻ and at $+254\text{ cm}^{-1}$ for KBr:SD⁻, see Fig. 2. This feature is analogous to lines found at roughly the same frequency for OH⁻ and OD⁻ [2] in alkali halides and for SH⁻ [4] in cesium halides, attributed to librations of the diatomics. The measured $\sqrt{2}$ isotope effect supports an identical interpretation for the line observed here. Similarly, a broad mode, which we identify as a libration, is found at $\nu_{\text{lib}} \approx 300\text{ cm}^{-1}$ higher frequency than ν_{01} (and, in the case of KCl, as a side band of the overtone, ν_{02} , as well) for SH⁻ in KCl and KI.

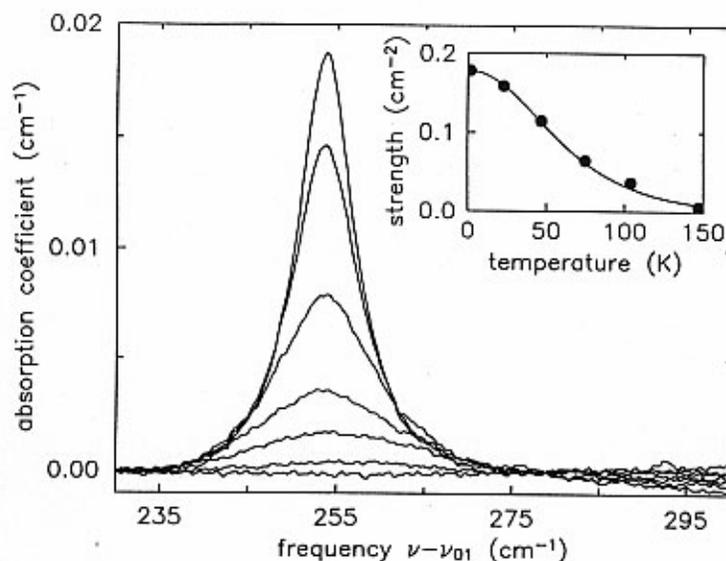


Fig. 2. Librational sideband of nominally KBr + 0.5 mol% KSD as a function of temperature at 1 cm^{-1} resolution. The main graph shows the high-frequency sideband for temperatures of 1.7, 23, 47, 75, 104, 147 and 293 K, from top to bottom. The integrated absorption strength of the side band, given by the solid dots on the inset graph, falls toward zero; the solid line on this inset plot is a fit to a phonon-coupling model, as explained in the text.

Given the librational frequency, ν_{lib} , and using the gas-phase value of the rotational constant, we can estimate the size of the reorientational potential barriers using the Devonshire model. This gives $|K| \cong 900\text{ cm}^{-1}$ for the barrier heights of SH^- and SD^- in the potassium halides, corresponding to a temperature of 1300 K. In light of this, it is very surprising to discover that the strength of the SD^- librational mode disappears at temperatures much less than this, see the inset plot of Fig. 2. A similar temperature dependence is also found for the SH^- librational side bands in a variety of different alkali halides. This is all the more surprising in that Klein et al. [2] claim that the strength of the librational sideband for OH^- actually *increases* with temperature. However, since the mode broadens rapidly with temperature, it is possible that they may have confused its strength with that of the underlying phonon-induced background; we plan to remeasure the OH^- side band strengths at various temperatures using a Fourier-transform interferometer.

What can account for our observed temperature dependence? First, note that the reorientational potential cannot have any significant temperature

dependence, since the librational frequency does not vary with temperature (cf. Fig. 2). Thermal depopulation of the ground state, assuming a two-dimensional anharmonic oscillator, gives rise to a 16% reduction in the line strength of the mode at 150 K [5], clearly not enough to explain the data. We have been able to fit the temperature dependence of the strength by coupling the libron to a Debye spectrum of phonons, using Eq. (15) of Ref. [5]. The result is graphed by the solid line in the inset plot of Fig. 2, with fit parameters $\theta_c = 230\text{ K}$ (not too different than the pure KBr Debye temperature, $\theta_D = 173\text{ K}$) and average coupling coefficient $\bar{A} = 1990\text{ cm}^{-1}$. However, this value of the coupling coefficient is unrealistically large: Otto [4] has measured the stress-induced shifts in the librational mode of CsBr: SH^- , which can be used to estimate $\bar{A} = 142\text{ cm}^{-1}$, more than an order of magnitude smaller. A larger coupling strength does result if the libron exchanges strength with a single mode of frequency Ω , rather than a spectrum of lattice modes; however, we would then expect to see side bands on the librational line at $\pm\Omega$. Hence, these explanations in terms of couplings to other

modes are untenable. The most likely remaining possibility is that our estimate of the barrier height is somewhat too large, so that the molecule is actually able to hop across a saddle point in the Devonshire potential. If this hopping is sufficiently rapid, then one can no longer speak meaningfully of a librational frequency.

We tentatively conclude that at low temperatures (or equivalently, low energies) the librational levels of the potential are occupied, but at higher temperatures hopping modes and, ultimately, nearly-free rotations of the defect will dominate. By measuring the temperature dependence of T_1 , it should be possible to determine the order of the decay process involved. This can then be compared to the observed variation of T_1 with the host lattice and defect.

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